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U.S. DEPARTMENT OF ENERGY
Conservation and Solar Energy
Office of Transportation Programs

Prepared for

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INTRODUCTION

In the experiments reported here, measurements were made at four axial positions downstream of a catalytic reactor to determine what effect the length available for gas-phase reactions downstream of a catalytic reactor has on carbon monoxide and unburned hydrocarbons emissions.

Experimental catalytic combustors have demonstrated the capability of achieving stable combustion with very lean fuel-air mixtures and with negligible amounts of thermal NO_x formation (refs. 1-14). However, the temperature range over which efficient combustion with low emissions can be obtained is limited on the high end by the maximum temperature that the catalyst can tolerate, and on the low end by the maximum allowable unburned hydrocarbons (UHC) and carbon monoxide (CO) emissions. Design of a catalytic combustor thus requires a knowledge of the effects of catalytic-reactor geometric variables as well as operating parameters on emissions characteristics.

For successful low-emissions operation, catalytic combustion must involve reactions both at the catalytic surface and in the gas phase (refs. 8, 9, 13, 15, 16). Combustion begins at the catalytic surface, and the stream temperature increases due to heat transfer from the surface. The catalytic rate of reaction is limited by the rate of diffusion of reactants to the surface and products from the surface. Eventually the gas-phase reactions are initiated, and they proceed at a much higher rate than the surface reactions to permit complete combustion in reasonably-sized combustors. Although the kinetics of high-temperature oxidation at catalytic surfaces have not been studied as extensively as gas-phase combustion, the available experimental evidence (ref. 17) shows that most hydrocarbons, including propane, convert into CO_2 and H_2O at the surface without forming CO. In contrast, the gas-phase combustion of lean fuel-air mixtures is well understood (ref. 18) to proceed by first oxidizing the hydrocarbon into CO and H_2O or H_2 . The intermediates CO and H_2 will then continue to react to form CO_2 and H_2O . Clearly then, the existence of CO in the products of a catalytic reactor is evidence of gas-phase reactions.

Although previous studies have evaluated the effects of monolithic catalyst cell density and reactor length on combustion performance (ref. 6), little information is available regarding the history of the pollutants UHC and CO downstream of the catalyst. The present work reports measurements of UHC and CO concentrations as a function of distance downstream of a catalytic reactor. Tests were performed using a 12-cm diameter by 11-cm long

monolithic catalytic reactor. The premixed propane-air feed had an equivalence ratio range of 0.14 to 0.24. The inlet-air temperature was 800 K, reference velocity (approach velocity at the catalytic-reactor inlet face), 10 m/s, and pressure, 3 and 6×10^5 Pa. Emissions concentrations were measured on the duct centerline at four axial positions between 0 and 22 cm downstream of the catalytic-reactor exit plane. The study was performed as supporting research for the DOE-sponsored Gas Turbine Highway Vehicle Systems Project which is administered by NASA Lewis.

APPARATUS AND PROCEDURE

The test section is shown in figure 1. It was made by inserting 12-cm inside-diameter by 15.2-cm outside diameter Carborundum T30R Fiberfrax tube insulation into the 15.2-cm inside diameter stainless-steel pipe.

Inlet air was indirectly preheated to 800 K for all tests. All data were obtained with a reference velocity (velocity approaching the catalytic-reactor inlet plane) of 10 m/s and pressures of 3 and 6×10^5 Pa. Gaseous propane fuel was injected into the airstream through a multiple conical-tube fuel injector developed by Tacina (refs. 19, 20). Equal amounts of gaseous propane fuel were injected into the small-diameter ends of each of 21 conical air passages. Good initial fuel dispersion was thereby assured. The injector was located 25 cm upstream of the catalytic reactor to insure good mixing and a uniform fuel-air ratio profile.

The catalytic reactor (see table 1) consisted of 4 12-cm diameter and 2.5-cm thick honeycomb monolithic catalyst elements stacked in series. The elements were identical and are described in table 1. Elements were separated by 0.317-cm-diameter thermocouple sheaths. The thermocouples were used to monitor temperatures along the reactor length.

Exhaust products from the catalytic reactor were sampled on the duct centerline at 4 axial positions: 0, 7, 17, and 22 cm downstream of the reactor exit plane. The sampling probes were 0.635 cm in outside diameter and were water cooled. The two major design considerations were (1) to provide sufficient flow area to avoid high sample pressure loss, and (2) to provide a large surface area for a high rate of heat transfer from the sample to the cooling water (for rapid quenching of the reactions in the sample stream). These objectives were met by using two sampling passages of 0.059-cm inside diameter at each probe entrance. Preliminary tests made with probes successively removed showed that no probe affected the sample obtained at downstream locations. The four probes were connected to a single sample line with valves to permit the selection of one sampling location at a time.

The continuous-flow sample passed through an electrically heated 0.625-cm diameter stainless-steel line to the on-line gas-analysis equipment. The sample-line temperature was maintained at 410-450 K. The gas-analysis equipment included a flame-ionization detector for unburned hydrocarbons and nondispersive infrared analyzers for CO and CO₂. Nitrogen oxides were not measured for this study. They have been shown in previous studies to be below measurable levels for catalytic combustion of propane fuel (refs. 3-6).

The equivalence ratio was determined both by metering the flowrates of fuel and air and by making a carbon balance from the measured concentrations of UHC, CO, and CO₂. The equivalence ratios reported are those determined by the carbon-balance method which differed only by 2-4 percent from the metered values. Adiabatic combustion temperatures were computed from these

carbon-balance equivalence ratios and the inlet-air temperature using a combustion-equilibrium computer program (ref. 21).

Emission concentrations were measured in ppm by volume. The results will be reported in terms of emission indexes which were computed from the concentrations using the relationship.

$$E_x = C_x \times 10^{-3} \frac{1 + f}{f} \frac{M_x}{M_p} \quad (1)$$

where

E_x emission index of specie x, g_x/kg fuel
 C_x concentration of specie x, ppmV
 f fuel-air weight ratio, (kg/s) fuel/(kg/s) air
 M_x molecular weight of specie x, $g_x/mole_x$
 M_p molecular weight of combustion products, $g_p/mole_p$

RESULTS AND DISCUSSION

The emission indexes computed from equation (1) using measured CO and HC concentrations are given in figures 2-5. NO_x emissions have been shown in previous catalytic combustion studies using propane to be of negligible levels (refs. 3-5, 13) and were not measured in this study. The inlet-air temperature and reference velocity for all tests reported were 800 K and 10 m/s.

Figure 2 shows the effect of equivalence ratio on CO (fig. 2(a)) and UHC (fig. 2(b)) emission indexes at a pressure of 3×10^5 Pa. At this condition, exhaust products from the catalytic reactor were sampled at three downstream positions: (1) at the reactor exit plane, (2) 7 cm downstream from the exit plane, and (3) 22 cm downstream. Separate curves are shown for each of these three locations.

Data were taken during two separate test runs. The test section had been dismantled between the two tests to permit the use of the rig for other experiments. On reconstruction, repeat data were obtained. The original and repeat data are distinguished in figure 2 by open and solid symbols.

At the catalytic-reactor exit plane, CO emissions (fig. 2(a)) increased monotonically as the equivalence ratio was increased from 0.14 to 0.22. Because surface reactions probably don't produce CO, the existence of high levels of CO at the catalyst exit plane is evidence of the contribution of gas-phase reactions in the combustion of the fuel. For sampling positions of 7 and 22 cm downstream, CO emissions first increased to a peak value of about 300 g CO/kg fuel, then decreased as the equivalence ratio was increased from 0.14 to 0.22. The maximum value of the CO emission index occurred at a 0.15 equivalence ratio at the 22-cm sampling distance and at a 0.18 equivalence ratio at the 7-cm distance.

Figure 2(b) gives the unburned hydrocarbons emission index. Values higher than about 100 g HC/kg fuel are not shown because the hydrocarbon analyzer became non-linear and eventually saturated for concentrations corresponding to this level. The trends indicated by the data are shown by dashed lines extending the data curves, however.

Unburned hydrocarbons emissions decreased monotonically with increasing equivalence ratio for all three sampling probe locations. Hydrocarbons emissions also decreased with distance from the reactor. At an equivalence ratio of 0.22, for example, emissions decreased two orders of magnitude in 22 cm.

These results show that downstream of the catalyst, where only gas-phase reactions could occur, fuel was still being converted to CO, and CO eventually oxidized to CO₂. Clearly, the length of the gas-phase region downstream of the catalytic reactor is an important design parameter, and significant performance and emissions benefits can be realized if the length of this region is increased. For example, in applications which have limits on the maximum CO and HC emissions, the catalytic reactor may be operated at leaner equivalence ratios if a longer gas-phase-reaction length is provided.

Figure 3 shows emissions at a pressure of 6×10^5 Pa as a function of equivalence ratio at an inlet temperature of 800 K and a reference velocity of 10 m/s. Emissions were determined at distances of 0, 7, 17, and 22 cm downstream of the catalyst.

CO emissions are given in figure 3(a) and show the same trends as were seen in the 3×10^5 -Pa results of figure 2(a). Peak CO emissions at each of the 4 probe positions were about 500 g/kg. The maximum CO level occurred at leaner equivalence ratios as the sampling position moved further downstream from the catalyst exit plane.

The unburned hydrocarbons emissions of figure 3(b) decreased monotonically with increasing equivalence ratio until a level of approximately 1 gHC/kg. fuel was reached. No further reduction was measured when either the probe distance or the equivalence ratio was increased. This result is probably an indication of background HC levels entering the analyzer from a sampling line containing some hydrocarbons from previous experimentation.

The trend of decreasing emissions with increasing distance from the catalytic reactor can be seen in figure 4 in which the 6×10^5 -Pa data used for figure 3 has been replotted as a function of distance to the sampling probe. Results are given for three equivalence ratios: 0.18, 0.21 and 0.23.

The CO emissions of figure 4(a) show the expected trend of decreasing levels with distance from the catalytic reactor once the highest value has been achieved. At an equivalence ratio of 0.18, the CO emission index continued to increase for distances up to 22 cm from the catalytic reactor. At an equivalence ratio of 0.21, CO emissions increased for distances up to about 5 cm from the catalytic reactor, then began to decrease. At an equivalence ratio of 0.23, the maximum CO occurred inside the catalytic reactor, and a monotonic decrease occurred downstream. These results are indicative of the higher reaction rates which occur as the equivalence ratio (and thus combustion temperature) is increased.

As expected, the unburned hydrocarbon emissions of figure 4(b) show a monotonic decrease with distance from the catalytic reactor.

The emissions obtained at the two pressures tested, 3×10^5 Pa and 6×10^5 Pa, are compared in figure 5. Figure 5(a) presents the comparison for the CO emissions and 5(b) for the HC emissions. Again, the emission index is given as a function of the distance from the catalytic-reactor exit plane. The 6×10^5 -Pa results are shown with open symbols and the 3×10^5 -Pa with solid symbols. Circular symbols represent data taken at 0.18 equivalence ratio, and diamond-shaped symbols, that at 0.21.

Figure 5(a) shows that the CO emissions peaked farther downstream for a pressure of 6×10^5 Pa than for 3×10^5 Pa with equivalence ratios of both 0.18 and 0.21. Similarly, figure 5(b) shows that generally higher levels of unburned hydrocarbons were observed at the higher pressure. Because the gas-phase reaction rate can be expected to increase with pressure, the results suggest that the initiation of gas-phase reactions occurred later in the reactor when the pressure was increased. In other words, at the higher pressure, the initial catalytic processes necessary for initiation of gas-

phase reactions could not have been as rapid. If more distance (and, therefore, residence time) had been provided for gas-phase reactions downstream of the reactor, it would be expected that ultimately both CO and HC would be lower at 6×10^5 Pa than at 3×10^5 Pa.

An increase in inlet temperature can be expected to result in an earlier initiation of gas-phase reactions, and would, therefore, have the same effect as increasing the distance available for gas-phase reactions downstream of the catalytic reactor. With an inlet temperature that was high enough, then, the emissions at 6×10^5 Pa would be lower than those at 3×10^5 Pa. In fact, it was reported in reference 7 that although emissions were higher at 6×10^5 Pa than at 3×10^5 Pa for inlet temperatures of 800 and 900 K, they were lower at 6×10^5 Pa for an inlet temperature of 1000 K.

CONCLUDING REMARKS

The results of this study demonstrated that the gas-phase oxidation of CO and UHC downstream of a catalytic reactor has a significant effect on the emissions produced by a catalytic combustor. At 800-K inlet-air temperature and 10-m/s reference velocity, emissions of both CO and UHC were found to decrease as much as two orders of magnitude over a gas-phase length of 22 cm. Because the pressure loss across the gas-phase region is very low compared with that across the catalytic reactor, it may be advantageous to achieve required levels of emissions through the replacement of some catalytic-reactor length with additional length in the gas-phase region downstream. It is possible that a decrease in catalytic reactor volume may also result in faster transient response. The length available for gas-phase oxidation has been shown here to be an important catalytic-combustor design parameter, but the trade-off between downstream gas-phase length and catalytic-reactor length needs to be studied in detail.

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TABLE 1

CATALYTIC REACTOR DESCRIPTION

Element Size.....	12 cm dia x 2.5 cm
Number of Elements.....	4
Catalyst.....	Pt/Pd: 1/1
Loading.....	9.5 kg/m ³
Catalyst Manufacturer.....	W. R. Grace & Co.
Substrate Material.....	Mullite
Cell Size.....	1.6 mm Round
Open Area.....	67 Percent
Substrate Manufacturer....	General Refractories

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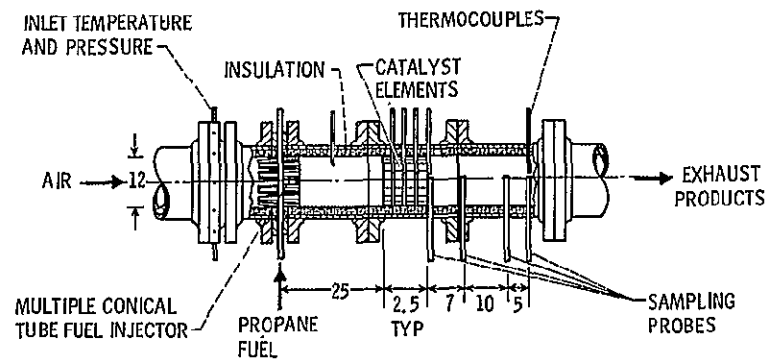
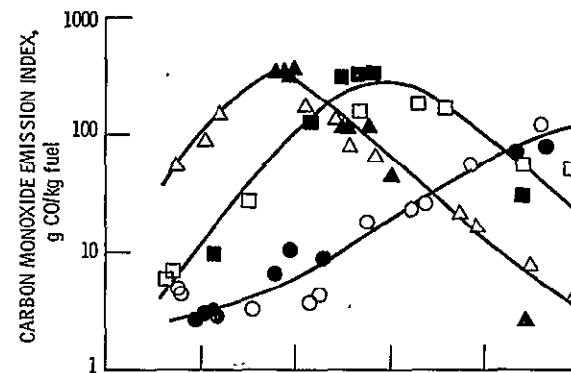
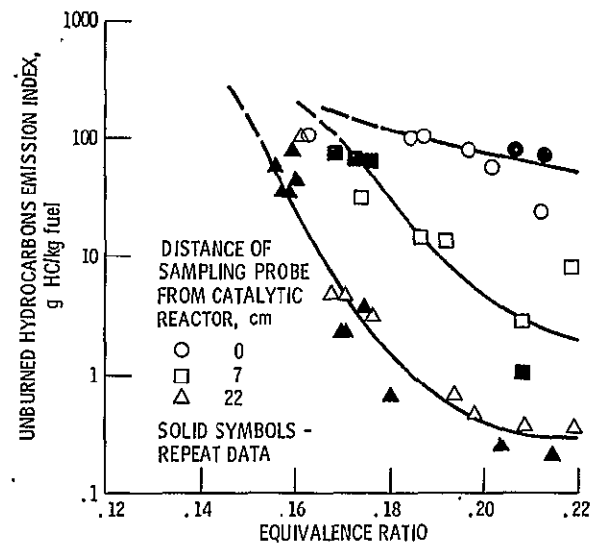


Figure 1. - Catalytic reactor test section. Dimensions are in cm.

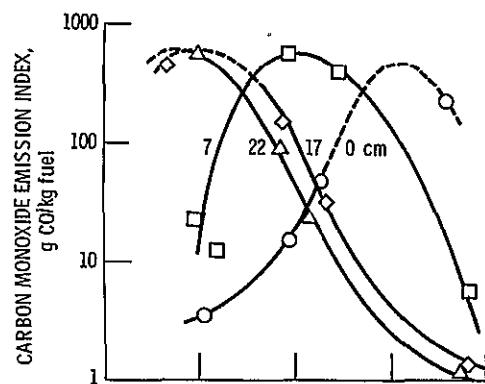


(a) Carbon monoxide emissions.

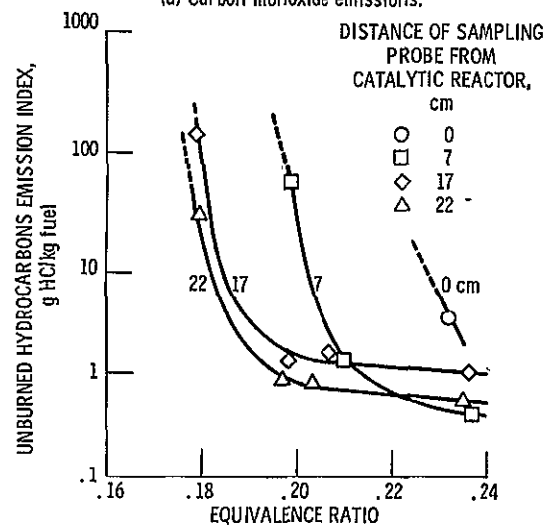


(b) Unburned hydrocarbons emissions.

Figure 2. - Effect of equivalence ratio on emissions at 3×10^5 Pa. inlet-air temperature, 800 K; Reference velocity, 10 m/s.

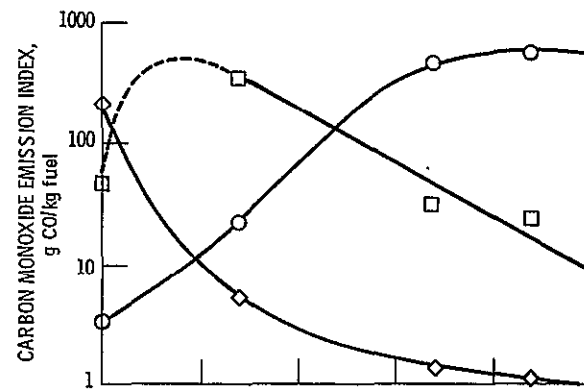


(a) Carbon monoxide emissions.

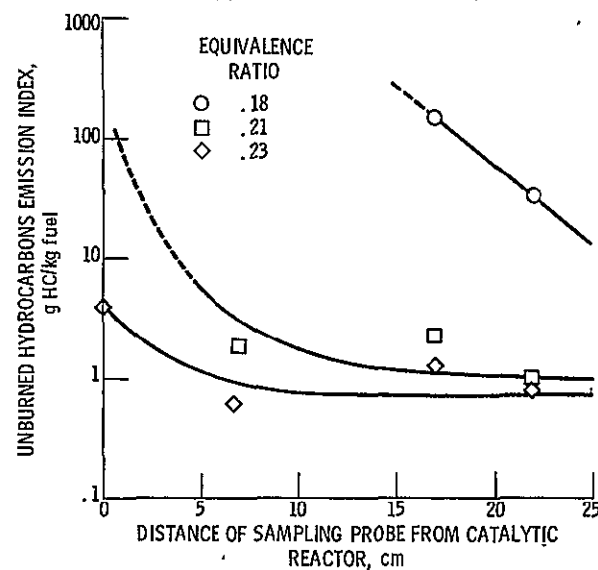


(b) Unburned hydrocarbons emissions.

Figure 3. - Effect of equivalence ratio on emissions at 6×10^5 Pa. Inlet-air temperature, 800 K; Reference velocity, 10 m/s.



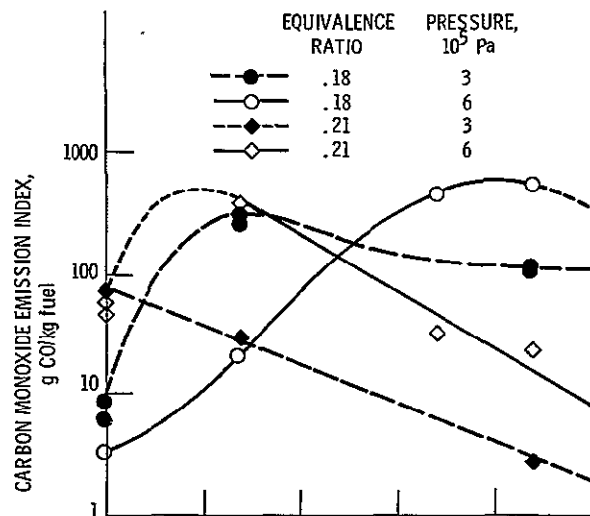
(a) Carbon monoxide emissions.



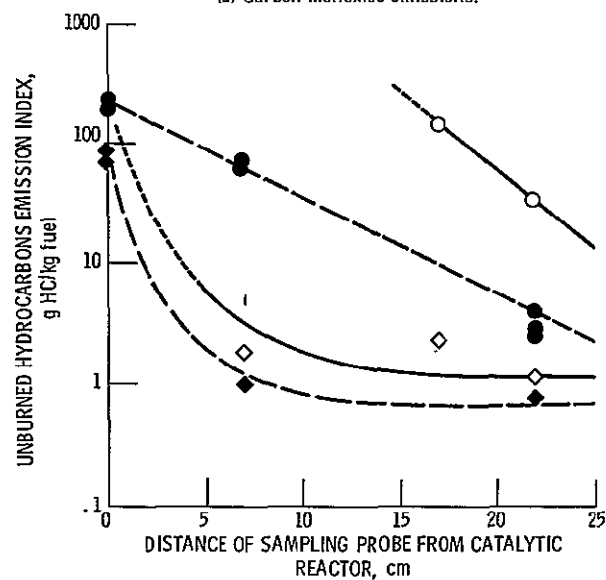
(b) Unburned hydrocarbons emissions.

Figure 4. - Effect of downstream reaction distance on emissions at 6×10^5 Pa. Inlet-air temperature, 800 K; Reference velocity, 10 m/s.

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(a) Carbon monoxide emissions.



(b) Unburned hydrocarbons emissions.

Figure 5. - Comparison of emissions at 3×10^5 Pa and 6×10^5 Pa. Inlet-air temperature, 800 K; Reference velocity, 10 m/s.

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16. Abstract The objective of the experiments reported here was to determine what effect the length available for gas-phase reactions downstream of the catalytic reactor has on the emissions of CO and unburned hydrocarbons. The work was performed as part of the DOE-supported Gas Turbine Highway Vehicle Systems Project. A premixed, prevaporized propane/air feed to a 12-cm-diameter catalytic-reactor test section was used. The catalytic reactor was made of four 2.5-cm-long monolithic catalyst elements. Four water-cooled gas-sampling probes were located at positions between 0 and 22 cm downstream of the catalytic reactor. Measurements of unburned hydrocarbons, CO, and CO ₂ were made. Tests were performed with an inlet-air temperature of 800 K, a reference velocity of 10 m/s, pressures of 3 and 6×10 ⁵ Pa, and fuel-air equivalence ratios of 0.14 to 0.24. For very lean mixtures, hydrocarbon emissions were high and CO continued to be formed downstream of the catalytic reactor. At the highest equivalence ratios tested, hydrocarbon levels were much lower and CO was oxidized to CO ₂ in the gas-phase downstream. To achieve acceptable emissions, a downstream region several times longer than the catalytic reactor could be required.					
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